1. According to the Third Law of Thermodynamics, the entropy of a perfect crystal is zero at $T = 0$. Adding heat increases the entropy. (Recall $dS = dq_{rev}/T$.) As a result, the entropies of substances calculated using the Third Law are always **positive**. (See, for example, Table 4.1).

    The entropies of several aqueous ions listed in Table 10.1 are **negative**, such as $S_m(Ca^{2+}, aq) = -53.1$ J K^{-1} mol^{-1} at 25 °C. Is this a violation of the Third Law? Explain.

2. Why do significant deviations from ideal behavior generally occur at lower concentrations for electrolyte solutions than for nonelectrolyte solutions?

3. Debye-Huckel (DH) theory gives

    $$\ln \gamma_+ = -1.173 z_+^2 \sqrt{I}$$

    $$\ln \gamma_- = -1.173 z_-^2 \sqrt{I}$$

    for the activity coefficients of aqueous cations and anions at 25 °C. Show (*hint*: $v_+z_+ + v_-z_- = 0$) that the mean ionic activity coefficient is

    $$\ln \gamma_\pm = -1.173 z_+ |z_-| \sqrt{I}$$

4. One of many important applications of ion activities is the pH, defined as the negative logarithm (base 10) of the activity of hydrogen ions.

    $$pH = -\log_{10}(a_{H+})$$

    But it's *impossible* to measure the pH defined in this manner! Why?

5. Practical pH measurements are made relative to a scale of pH values assigned to a series of reference solutions, such as pH 1.096 for 0.100 mol kg^{-1} aqueous HCl solutions at 25 °C.

   **a)** Potentiometric measurements for the following solutions on opposite sides of a membrane permeable to H$^+$ ions give $\phi_{Right} - \phi_{Left} = -0.027$ volt at 25 °C. Calculate the pH of the solution on the right.

Left Side	Right Side
0.100 mol kg^{-1} HCl (reference)	test solution
pH 1.096	pH ?

    b) Why don't the H$^+$ ions diffuse from the side with the lower pH to the side with the higher pH (from higher to lower activity) to reach equilibrium (*i.e.*, equal activities on both sides)?

6. **a)** Calculate the pH of a 0.100 mol kg^{-1} solution of HCl assuming the solution is ideal.

b) Recalculate the pH of a 0.100 mol kg^{-1} HCl solution using $\ln \gamma_+ = -1.173 z_+^2 \sqrt{I}$ from DH theory to allow for nonideal solution behavior.

c) Using DH theory, calculate the pH of a solution containing 0.100 mol kg^{-1} HCl and 0.500 mol kg^{-1} LaCl$_3$.

d) Notice that the pH depends on more than just the H^+ concentration. *Why?*

**7.** The freezing point depression of a 0.100 mol kg^{-1} solution of aqueous dichloroacetic acid is 0.279 °C. Assuming the solution is ideal and using $K_f = 1.86$ K kg mol^{-1}, calculate the equilibrium constant for the dissociation of the acid

$$HCl_2CCOOH(aq) \quad = \quad H^+(aq) \quad + \quad HCl_2CCOO^-(aq)$$
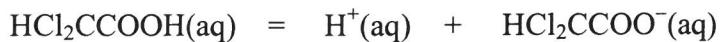
8. Assuming ideal solutions, calculate the solubility of Ba(OH)$_2$ at 25 °C ($K_{sp} = 0.0050$) in

a) water
b) 0.200 mol kg^{-1} aqueous NaCl solution
c) 0.200 mol kg^{-1} aqueous BaCl$_2$ solution. Why is this solubility significantly lower?

9. Using DH theory, calculate the solubility of Ba(OH)$_2$ at 25 °C ($K_{sp} = 0.0050$) in

a) water
b) 0.200 mol kg^{-1} aqueous NaCl solution
c) Is the solubility of Ba(OH)$_2$ significantly affected by nonideal solution behavior?

10. **a)** Calculate the equilibrium constant for the following reaction at 25 °C:

$$Cu^{2+}(aq) \quad + \quad Zn(s) \quad = \quad Cu(s) \quad + \quad Zn^{2+}(aq)$$
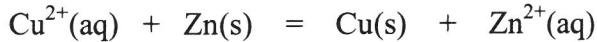
Data: $\Delta G_{fm}°(Cu^{2+}, aq) = 65.5$ kJ mol^{-1} $\qquad$ $\Delta G_{fm}°(Zn^{2+}, aq) = -147.1$ kJ mol^{-1}

b) A 0.250 mol kg^{-1} CuSO$_4$ solution is poured onto a sheet of zinc metal. Assuming ideal solution behavior, calculate the molalities of Cu^{2+} and Zn^{2+} ions at equilibrium. Why does the zinc appear to turn gray? Can you suggest a chemical treatment for the quantitative removal of copper ions from water?

Chem 232   Tutorial #2

① $S_m(Ca^{2+}, aq) = -53.1$ J K^{-1} mol^{-1} and other
tabulated ionic entropies that are negative are
not violations of the Third Law.

The ionic entropies are not absolute entropies. They
are arbitrarily defined relative to $S_m(H^+, aq)$
set equal to zero, not equal to absolute entropy
of a perfect crystal at $T = 0$ equal to zero.

(not a pure compound)

Also, ions in solution can't be a perfect crystal,
so Third-Law entropy calculations do not apply.

---

② Ions interact electrically over much longer ranges
than the short range dipole-dipole interactions
of neutral molecules.

Also   charge-charge interactions are stronger
than dipole-dipole interactions.

---

③ neutral electrolyte $C_{\nu_+} A_{\nu_-}$

C^{z+} Cation

A^{z-} anion
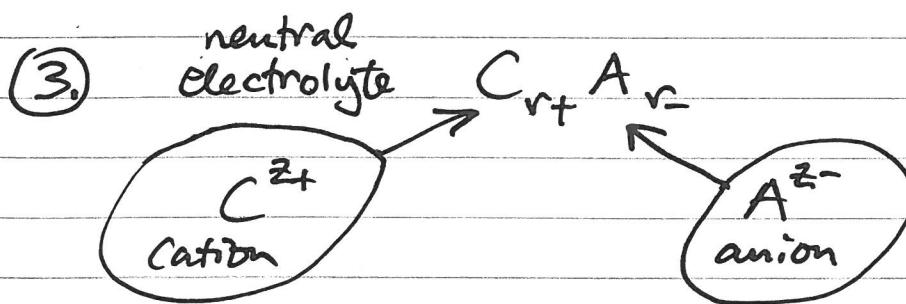
example:
$CaCl_2$
$z_+ = 2$ $z_- = 1$
$\nu_+ = 1$ $\nu_- = 2$

electroneutrality requires $\nu_+ z_+ + \nu_- z_- = 0$

absolute value:
$|z_-| = -z_-$

or

$\nu_+ z_+ = \nu_- |z_-|$

(3 cont.)

the <u>mean ionic activity coefficient</u> $\gamma_\pm$ is defined as

$$\gamma_\pm = \left(\gamma_+^{v_+} \gamma_-^{v_-} \right)^{\frac{1}{v_+ + v_-}} = \left(\gamma_+^{v_+} \gamma_-^{v_-} \right)^{\frac{1}{v}}$$

Why γ_+, γ_- and a <u>third</u> activity coefficient $\gamma_\pm$?

Because single-ion activity coefficients γ_+ and γ_- are not measurable, but $\gamma_\pm$ for the neutral electrolyte component $C_{v_+} A_{v_-}$ is measurable.

Debye and Huckel, from theory, derived
(DH)

$$\ln \gamma_+ = -1.173 z_+^2 \sqrt{I} \quad \text{and} \quad \ln \gamma_- = -1.173 z_-^2 \sqrt{I}$$

What is the DH prediction for the measurable mean ionic activity coefficient ?

$$\ln \gamma_\pm = \ln \left[\gamma_+^{v_+} \gamma_-^{v_-} \right]^{\frac{1}{v_+ + v_-}} = \frac{v_+}{v_+ + v_-} \ln \gamma_+ + \frac{v_-}{v_+ + v_-} \ln \gamma_- \quad \text{(definition)}$$

$$= \frac{v_+}{v_+ + v_-} (-1.173) z_+^2 \sqrt{I} + \frac{v_-}{v_+ + v_-} (-1.173) z_-^2 \sqrt{I} \quad \left(\begin{array}{c} \text{from DH} \\ \text{theory} \end{array} \right)$$

$$= - \left(\frac{v_+ z_+^2}{v_+ + v_-} + \frac{v_- z_-^2}{v_+ + v_-} \right) 1.173 \sqrt{I} \quad \left(\begin{array}{c} \text{use} \\ v_+ z_+ = - v_- z_- \end{array} \right)$$

$$= - \left(- \frac{v_- z_- z_+}{v_+ + v_-} - \frac{v_+ z_+ z_-}{v_+ + v_-} \right) 1.173 \sqrt{I} \quad \text{use } |z_-| = -z_-$$

$$= - \left(\frac{v_- z_+ |z_-| + v_+ z_+ |z_-|}{v_+ + v_-} \right) 1.173 \sqrt{I}$$

$$\boxed{\ln \gamma_\pm = -1.173 \, z_+ |z_-| \sqrt{I}}$$ useful only for very dilute solutions   see 00!

(4.) $\qquad pH \equiv -\log_{10}(a_{H^+})$

$\qquad\qquad = -\log_{10}(\gamma_{H^+} m_{H^+})$ $\qquad$ not practical

can't measure single-ion activity coefficients, such as γ_{H^+}!

H^+ ions are always found in combination with anions, such as Cl^-

can measure $\gamma_{\pm} = \sqrt{\gamma_{H^+} \gamma_{Cl^-}}$ for aqueous HCl, but $\gamma_{\pm}$ includes a contribution from the activity of the Cl^- ion, so, in general, $\gamma_{\pm} \neq \gamma_{H^+}$

(5.) a) $\qquad \phi_L \qquad\qquad\qquad \phi_R \qquad\qquad$ measure

$\qquad$ pH = 1.096 $\qquad\qquad$ pH = ? $\qquad\qquad \phi_R - \phi_L = -0.027 V$

$\qquad$ (assigned pH $\qquad\qquad\qquad\qquad$ relative to
$\qquad$ value, not $\qquad\qquad\qquad\qquad\qquad$ reference
$\qquad$ measured) $\qquad\qquad\qquad\qquad$ pH = 1.096
$\qquad$ for $0.100 \frac{mol}{kg}$ HCl

$$(\text{total } H^+ \text{ potential})_{Left} = (\text{total } H^+ \text{ potential})_{Right}$$

$$\left(\mu^0_{H^+} + RT \ln a_{H^+} + z_{H^+} F\phi\right)_{Left} = \left(\mu^0_{H^+} + RT \ln a_{H^+} + z_{H^+} F\phi\right)_{Right}$$

$$RT \ln a_{H^+ Left} + z_{H^+} F(\phi_{Left} - \phi_{Right}) = RT \ln a_{H^+ Right}$$

$$\ln a_{H^+ Right} = \ln a_{H^+ Left} + \frac{z_{H^+} F(\phi_{Left} - \phi_{Right})}{RT}$$

$$-\ln a_{H^+ Right} = -\ln a_{H^+ Left} + \frac{z_{H^+} F(\phi_{Right} - \phi_{Left})}{RT}$$

(5a cont.)

$$\log_{10} x = \frac{\ln x}{2.303} = \frac{\ln x}{\ln 10}$$

$$-\frac{\ln a_{H+ Right}}{2.303} = -\frac{\ln a_{H+ Left}}{2.303} + \frac{z_{H+} F(\phi_{Right} - \phi_{Left})}{2.303 \, RT}$$

$$\boxed{pH_{Right} = pH_{Left} + \frac{z_{H+} F(\phi_{Right} - \phi_{Left})}{2.303 \, RT}}$$

$$= 1.096 + \frac{(1)(96485 \; C \, mol^{-1})(-0.027 V)}{2.303 (8.314 \; J \, K^{-1} mol^{-1})(298.15 \; K)}$$

$$= 1.096 - 0.456$$

$$\boxed{pH_{Right} = 0.640}$$

b) $a_{H+} = 10^{-pH}$ (from $pH = -\log_{10} a_{H+}$)

| Left Side | Right Side |

$$a_{H+} = 10^{-1.096} = 0.080$$ $$a_{H+} = 10^{-0.640} = 0.229$$

+0.027 higher
electric potential

chemical diffusion
from higher to
lower H^+ activity

← (arrow pointing left)

ionic conduction
from higher
to lower
electric potential
energy

→ (arrow pointing right)

net H^+ flux (diffusion + conduction)
= 0   a balance is struck

6. a) $0.100 \text{ mol kg}^{-1}$ aqueous HCl $\longleftarrow$ <superscript>=</superscript>"strong" electrolyte

$$m_{H+} = 0.100 \text{ mol kg}^{-1}$$

$a_{H+} = \gamma_{H+} m_{H+}$ if the solution is ideal: $\gamma_{H+} = 1$

$$a_{H+} = m_{H+}$$

$$pH = -\log_{10} a_{H+} = -\log_{10} m_{H+} \quad (\text{if ideal})$$
$$= -\log_{10}(0.100)$$
$$= -(-1.00)$$

$\boxed{pH = \boxed{1.00}}$ assuming ideal solution behavior

b) recalculate the pH of $0.100 \text{ mol kg}^{-1}$ HCl using DH theory to include nonideal behavior

$$\ln\gamma_{H+} = -1.173 \, z_+^2 \sqrt{I} = -1.173(1)^2 \sqrt{\frac{z_{A+}^2 m_{H+} + z_{Cl-}^2 m_{Cl-}}{2}}$$

$$= -1.173 \sqrt{\frac{m_{H+} + m_{Cl-}}{2}} = -1.173 \sqrt{\frac{0.100 + 0.100}{2}}$$

$$\ln\gamma_{H+} = -0.371 \qquad \gamma_{H+} = e^{-0.371} = 0.690$$

$$pH = -\log_{10}(a_{H+}) = -\log_{10}(\gamma_{H+} m_{H+}) = -\log_{10}([0.690][0.100])$$

$\boxed{pH = \boxed{1.16} \text{ using DH theory for nonideal solutions}}$

c) pH of $0.100 \frac{\text{mol}}{kg}$ HCl + $0.500 \frac{\text{mol}}{kg}$ $LaCl_3$?

$$I = \frac{m_{H+} + m_{Cl-} + 9\,m_{La+++}}{2} = \frac{0.100 + 1.600 + 9(0.500)}{2} = 3.10$$

$$\ln\gamma_{H+} = -1.173\sqrt{I} = -2.06 \qquad \gamma_{H+} = 0.127 \quad \boxed{\begin{array}{c}\text{with}\\ 0.500\frac{\text{mol}}{kg} LaCl_3\end{array}}$$

$$pH = -\log_{10}(\gamma_{H+} m_{H+}) = -\log_{10}([0.127][0.100]) = \boxed{1.90}$$

d) a_{H+} and therefore pH depends on the $H+$ molality and on the activity coefficient γ_{H+} WHY? $\Rightarrow a_{H+} = \gamma_{H+} m_{H+}$

$$\boxed{\Delta T \neq K_f m \,!} \quad \begin{array}{c} HA \rightleftharpoons H^+ + A^- \\ (1-\alpha)m \quad \alpha m \quad \alpha m \end{array} \quad \begin{array}{l} \Delta T = K_f(m_{HA} + m_{H^+} + m_{A^-}) \\ \qquad = K_f(1+\alpha)m \end{array}$$

(Q7) dichloroacetic acid is a weak electrolyte,

only partially dissociated to H^+ and HCl_2CCOO^- ions

$$HCl_2CCOOH \rightleftharpoons H^+ + HCl_2COO^- \qquad \text{equilibrium constant } K$$
$$(1-\alpha)m \qquad\qquad \alpha m \qquad \alpha m$$
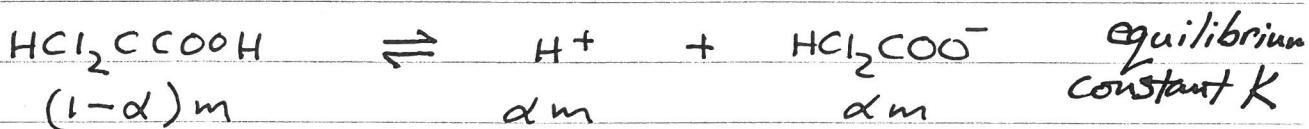
total acid molality $\quad m = m_{HCl_2CCOOH} + m_{HCl_2COO^-}$

$$\alpha = \frac{\text{extent of}}{\text{dissociation}} = \frac{\text{fraction of}}{\substack{\text{dissociated} \\ \text{acid molecules}}} = \frac{m_{HCl_2COO^-}}{m} = \frac{m_{H^+}}{m}$$

$$K = \frac{m_{H^+}\, m_{HCl_2COO^-}}{m_{HCl_2COOH}} = \frac{(\alpha m)(\alpha m)}{(1-\alpha)m} = \frac{\alpha^2 m}{1-\alpha}$$

(no activity coefficients – ideal solutions assumed)

freezing point depression (a colligative property) gives
the total number of solute molecules or ions

$$\Delta T = K_f \left(m_{HCl_2COOH} + m_{H^+} + m_{HCl_2COO^-} \right)$$

total molecular + dissociated acid molality

$$\Delta T = K_f \left[(1-\alpha)m + \alpha m + \alpha m \right] = K_f(1+\alpha)m$$

$$m = 0.100 \text{ kg mol}^{-1} \qquad \Delta T = 0.279 K \qquad K_f = 1.86 \text{ K kg mol}^{-1}$$

$$0.279 = 1.86(1+\alpha)0.100 \qquad\qquad \alpha = 0.500$$

$$K = \frac{\alpha^2 m}{1-\alpha} = \frac{(0.500)^2 \, 0.100}{1-0.500} = 0.050$$

(Q8) Solubility of $Ba(OH)_2$ assuming ideal solutions

$$K_{sp} = a_{Ba^{2+}}(a_{OH^-})^2 = m_{Ba^{2+}}(m_{OH^-})^2$$

a) $Ba(OH)_2$ in water   solubility $= m$ (ideal)

$$K_{sp} = m_{Ba^{2+}}(m_{OH^-})^2$$

$$Ba(OH)_2(s) \rightarrow Ba^{2+} + 2OH^-$$
$$ m \qquad 2m$$
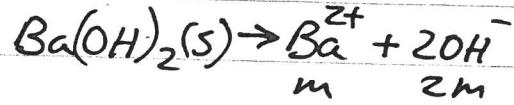
$$K_{sp} = m(2m)^2 = 4m^3$$

$$m = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{0.0050}{4}\right)^{1/3} = 0.108 \ \frac{mol}{kg}$$

b) $Ba(OH)_2$ in $0.200 \ mol \ kg^{-1}$ $NaCl$ solution

Same answer as part a! (assuming ideal solutions)

c) ⟨common ion⟩
    $Ba(OH)_2$ solubility in $0.200 \ mol \ kg^{-1}$ $BaCl_2$ solution
    (m) m_{BaCl_2}

(circled) Ba^{2+} from $BaCl$ reduces the $Ba(OH)_2$ solubility

$$m_{Ba^{2+}} = m + m_{BaCl_2}$$
from $Ba(OH)_2$ / from $BaCl_2$ $(0.200 \ mol \ kg^{-1})$

$$m_{OH^-} = 2m \quad \text{from } Ba(OH)_2$$

$Ba(OH)_2$ and $BaCl_2$ both have Ba^{2+} ions: reduces $Ba(OH)_2$ solubility m

$Ba(OH)$

$$K_{sp} = m_{Ba^{2+}}(m_{OH^-})^2 = (m + m_{BaCl_2})(2m)^2$$

$$\boxed{0.0050 = (m + 0.200)4m^2}$$ ← cubic equation in m solved on the next page

plot $(m + 0.200)4m^2 - 0.0050$ against m
$= 0$ at $m = 0.0682 \ mol \ kg^{-1}$

d) $Ba(OH)_2$ is less soluble in $BaCl_2$ solutions $\Rightarrow$ ⟨common ion effect⟩

$\boxed{Q8c}$ numerical solution of the cubic equation

$$0.0050 = (m + 0.200) 4m^2$$

plot $f(m) = (m + 0.200) 4m^2 - 0.0050$
against m
locate $m = 0.0682$ mol kg^{-1} where $f(m) = 0$

$f(m) = 0$ at $m = 0.0682$ mol kg^{-1}

x-axis: Ba(OH)$_2$ molality m / mol kg^{-1}

y-axis: $f(m) = (m + 0.200) 4m^2 - 0.0050$
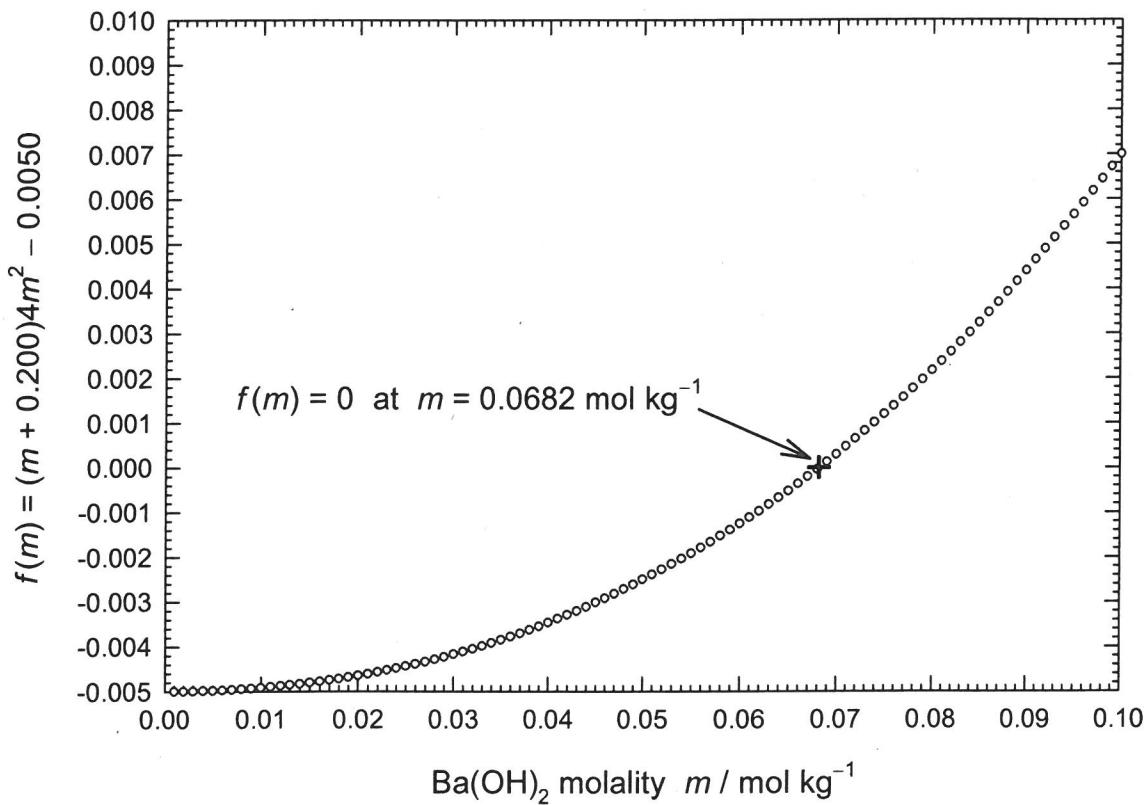
Ba(OH)$_2$ solubility in 0.200 mol kg^{-1} BaCl$_2$
$m = 0.0682$ mol kg^{-1}

$$Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq) \quad K = K_{sp}$$
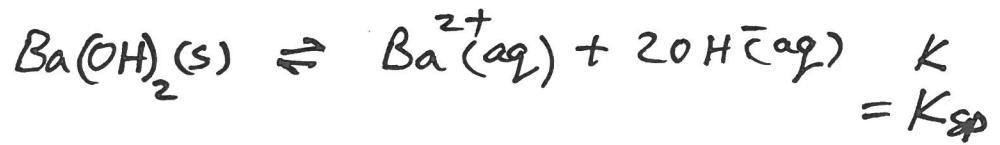
(Q9) Do not assume ideal solutions!

for aqueous $Ba(OH)_2$, use
(molality m)

$$K_{sp} = a_{Ba(OH)_2} = (a_{Ba2+})(a_{OH-})^2$$

$$= (\gamma_{Ba2+}\, m)(\gamma_{OH-}\, 2m)^2$$

$$= \gamma_{Ba2+}\, \gamma_{OH-}^2 \, 4m^3$$

can't measure γ_{Ba2+} or γ_{OH-}!

$$\boxed{K_{sp} = \gamma_\pm^3 \, 4m^3}$$

use mean ionic activity coefficient instead

estimate $\gamma_\pm$ using DH theory: $\ln\gamma_\pm = -1.173\,|z_+ z_-|\sqrt{I}$

$$z_+ = 2 \qquad z_- = -1 \qquad I = \frac{z_+^2 M_+ + z_-^2 M_-}{2}$$

$$\gamma_\pm = e^{\ln\gamma_\pm}$$

$$= \frac{(4)m_{Ba2+} + (1)m_{Cl-}}{2}$$

$$I = \frac{4m + 2m}{2} = 3m$$

$$\gamma_\pm = e^{-1.173(2)\sqrt{3m}}$$

$$\boxed{\gamma_\pm^3 = e^{-1.173(2)(3)\sqrt{3m}}}$$

Solve for m ($Ba(OH)_2$ solubility):

$$K_{sp} = \gamma_\pm^3 \, 4m^3 = \boxed{0.0050 = e^{-1.173(2)(3)\sqrt{3m}} \, 4m^3}$$

UH OH! another nonlinear equation

Solubility of $Ba(OH)_2$ (nonideal solution)

To solve $0.0050 = e^{-1.173(2)(3)\sqrt{3m}} \, 4m^2$

plot $f(m) = e^{-1.173(2)(3)\sqrt{3m}} - 0.0050$

to find m ($Ba(OH)_2$ solubility) at $f(m) = 0$

Problem !

f(m) never equals 0 !

no "root"

no m value

y-axis: $f(m) = e^{-1.173(2)(3)\sqrt{3m}} - 0.0050$

x-axis: $Ba(OH)_2$ molality m / mol kg^{-1}
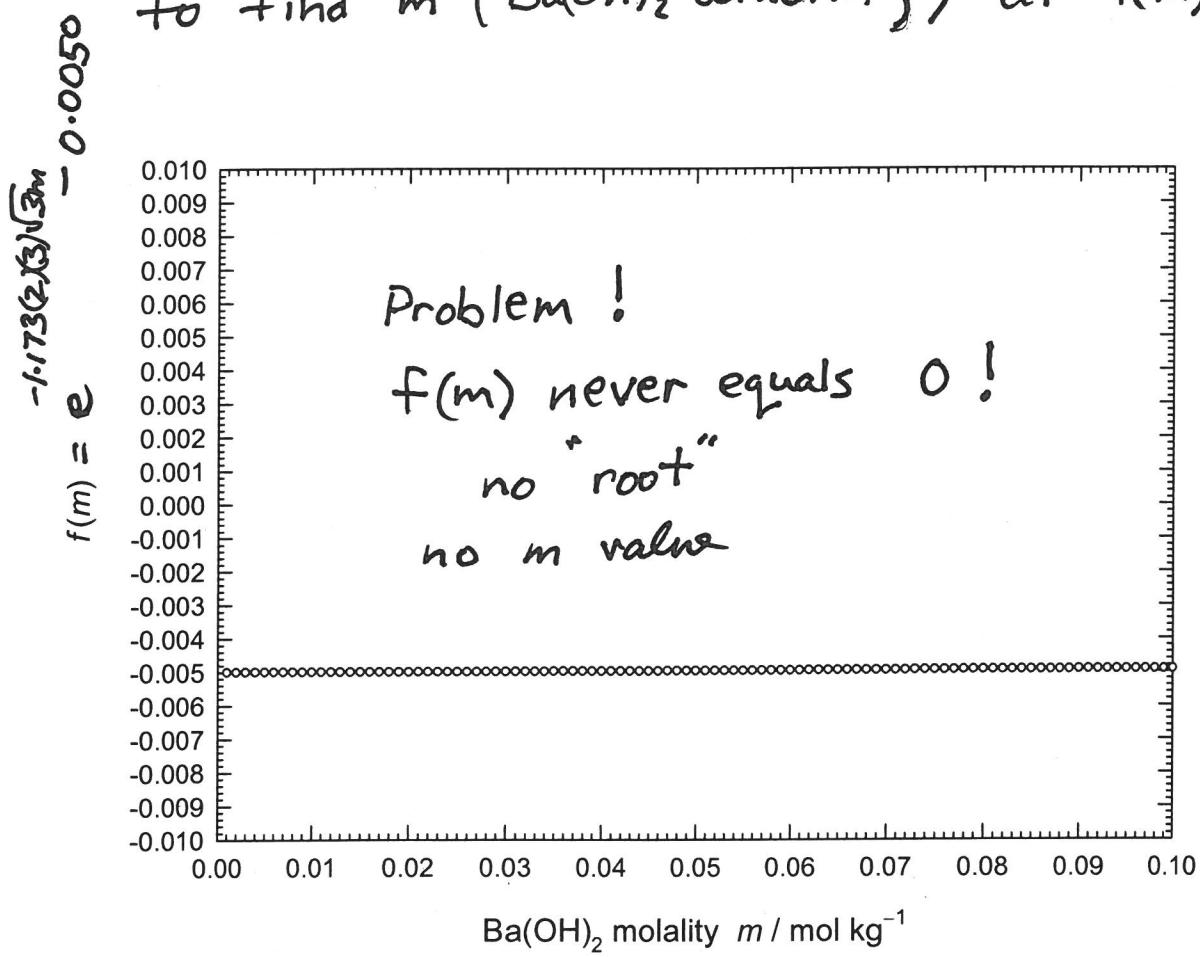
WHY? DH theory is being used for concentrated solutions where

$$\ln \gamma_\pm = -1.173 |z_+ z_-| \sqrt{I}$$

is not reliable.

A good lesson → don't push theory too far!

(Q9 a cont.)   what to do?

solubility of $Ba(OH)_2$ nonideal solution?

replace $\ln \gamma_{\pm} = -1.173 \, |z_+ z_-| \sqrt{I}$

with "extended" Debye Huckel theory: (more reliable at higher ionic strengths)

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \frac{\sqrt{I}}{1 + \sqrt{I}}$$ "new" denominator $1 + \sqrt{I}$

solve:

$$0.0050 = e^{-1.173(2)(3)\frac{\sqrt{3m}}{1+\sqrt{3m}}} \, 4m^2$$

plot:

$$f(m) = e^{-1.173(2)(3)\frac{\sqrt{3m}}{1+\sqrt{3m}}} \, 4m^3 - 0.0050 \quad \text{against } m$$

find root at $Ba(OH)_2$ solubility $0.355 \, \frac{mol}{kg}$

(9a cont.)

extended DH Theory

$$f(m) = e^{-1.173(2)(3)\frac{\sqrt{3m}}{1+\sqrt{3m}}} \; 4m^3 - 0.0050 \text{ against } m$$

Ba(OH)$_2$ solubility 0.355 mol kg^{-1}

$f(m) = 0$ at Ba(OH)$_2$ molality $m = 0.355$ mol kg^{-1}

(9 cont.) $Ba(OH)_2 (m) + NaCl (m_{NaCl} = 0.200 \text{ mol kg}^{-1})$
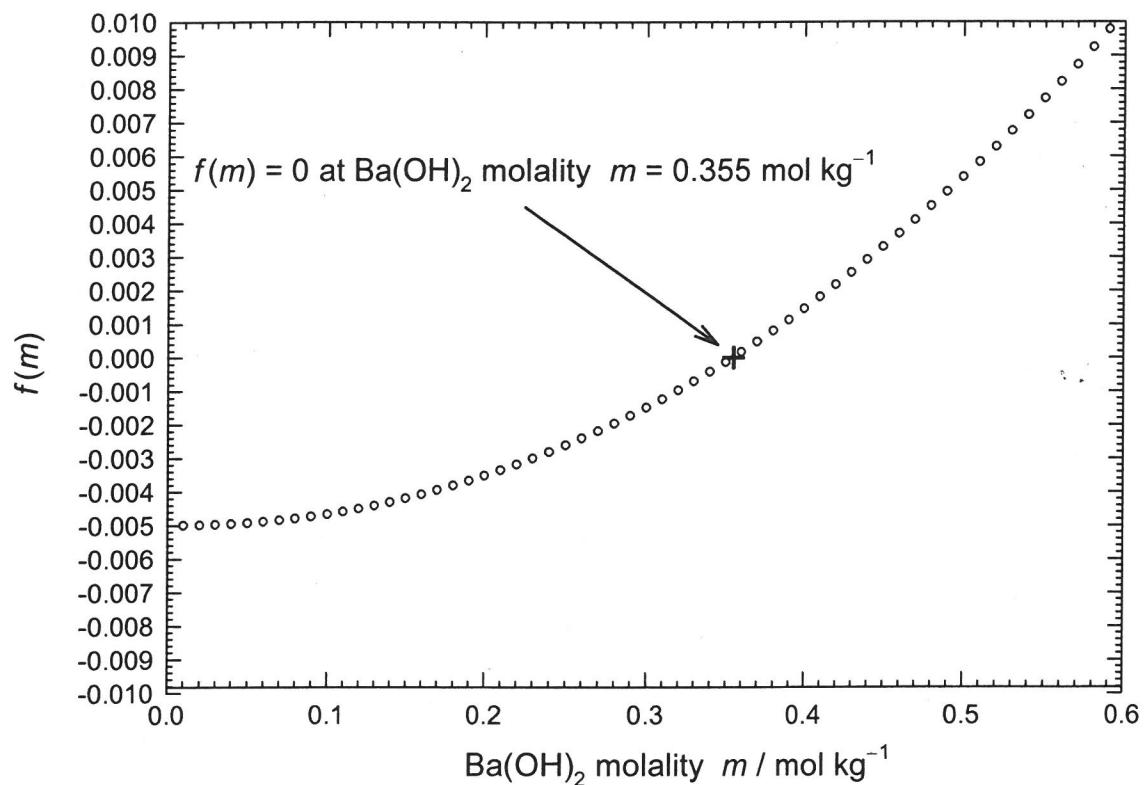
(m)

b) solubility of Ba(OH) in $0.200 \text{ mol kg}^{-1}$ NaCl solution predicted using extended DH theory:

<u>NaCl increases the ionic strength</u>

$$I = \frac{z_{Ba2+}^2 m_{Ba2+} + z_{OH-}^2 m_{OH-} + z_{Na+}^2 m_{Na} + z_{Cl-}^2 m_{Cl-}}{2}$$

$$= \frac{4m + (1)(2m) + (1)m_{NaCl} + (1)m_{NaCl}}{2}$$

$$I = 3m + m_{NaCl} = 3m + 0.200 \text{ mol kg}^{-1}$$

$$K_{sp} = a_{Ba2+} a_{OH-}^2 = \gamma_{\pm}^3 m(2m)^2$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \frac{\sqrt{I}}{1 + \sqrt{I}} \qquad \begin{array}{l} \text{extended DH} \\ \text{theory for } Ba(OH)_2 \end{array}$$

$$\gamma_{\pm} = e^{-1.173(2) \quad 3m+}$$

solve $\qquad 0.0050 = e^{-1.173(2 \times 3) \frac{\sqrt{3m+.200}}{1+\sqrt{3m+.200}}} \quad 4 m^3$

find (next page) $m = 0.375 \text{ mol kg}^{-1}$

c) Predicted $Ba(OH)_2$ solubility significantly affected by nonideal solution behavior:
in water: $0.068 \frac{mol}{kg}$ (ideal) $\underset{=}{or}$ $0.355 \frac{mol}{kg}$ (nonideal)

in $0.200 \frac{mol}{kg}$ NaCl : $0.068 \frac{mol}{kg}$ (ideal) $\underset{=}{or}$ $0.375 \frac{mol}{kg}$ (nonideal)

(9b) cont.)

Solubility of $Ba(OH)_2$ in $0.200 \frac{mol}{kg}$ NaCl

solve $f(m) = 0 = e^{-1.173 \frac{\sqrt{3m + .200}}{1 + \sqrt{3m + .200}} (2)(3)} \, 4m^3 - 0.0050$

(extended DH theory)

$f(m) = 0$ at $Ba(OH)_2$ molality $m = 0.375$ mol kg^{-1}
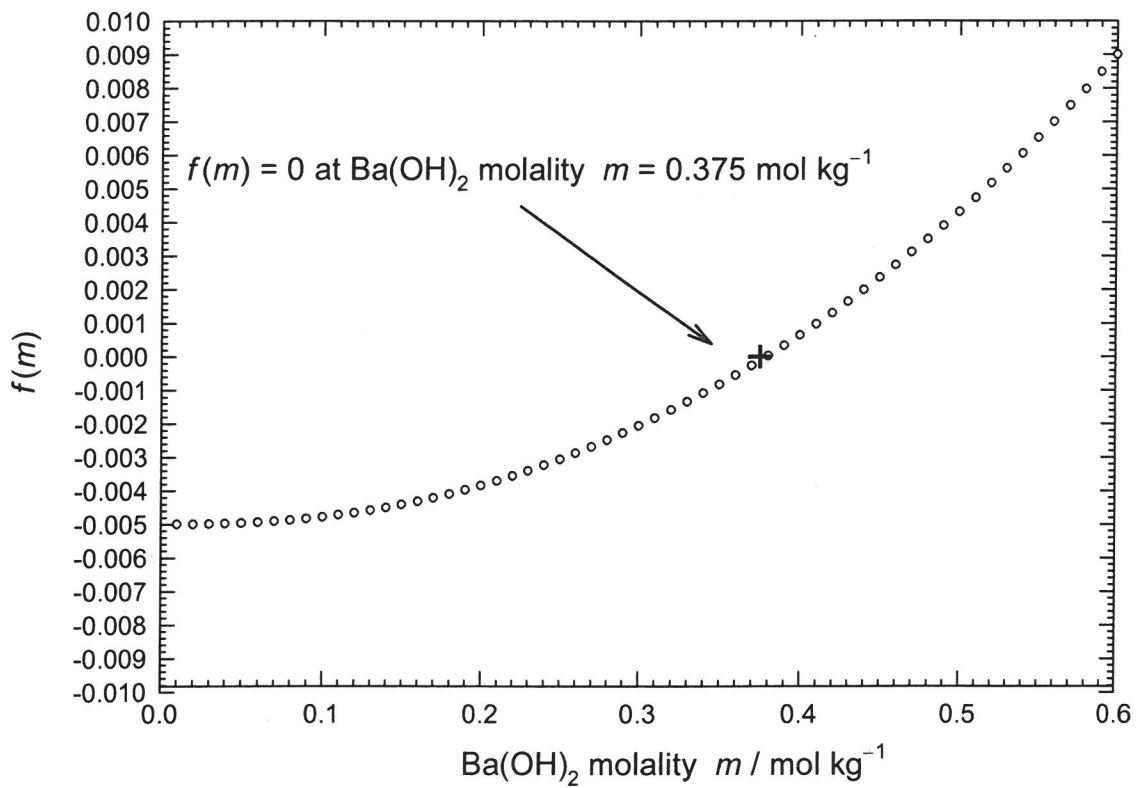
Adding NaCl increases the solubility of $Ba(OH)_2$ by increasing the ionic strength and therefore reducing $\gamma_{\pm}$.

("salting in" effect)

(10.) $Cu^{2+}(aq) + Zn(s) = Cu(s) + Zn^{2+}(aq)$ K

a) $\Delta G^\circ = \Delta G^\circ_{fm}(Cu, s) + \Delta G^\circ_{fm}(Zn^{2+}, aq) - \Delta G^\circ_{fm}(Cu^{2+}, aq) - \Delta G^\circ_{fm}(Zn, s)$

$= 0 + (-147.1) - (65.5) - 0$ kJ mol^{-1}

$\Delta G^\circ = -212.6$ kJ mol^{-1}

$K = \exp(-\Delta G^\circ / RT) = \exp(+212600 / (8.314)(298.15))$

$\boxed{K = 1.770 \times 10^{37}}$

b) $Cu^{2+}(aq) + Zn(s) = Cu(s) + Zn^{2+}(aq)$

initially: 0.250 mol kg^{-1} $\left(\begin{array}{c} \text{goes to} \\ \text{completion} \\ K \gg 1 \end{array}\right)$ 0.000 mol kg^{-1}

equilibrium 0.250 − x   0.000 + x
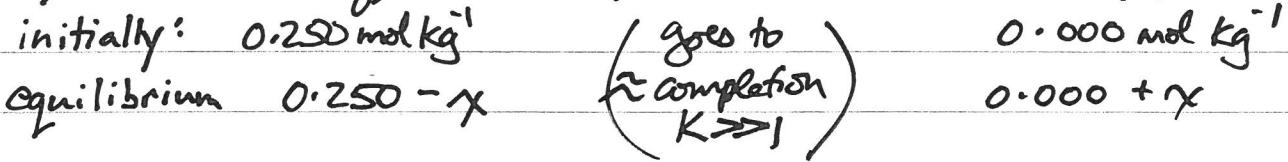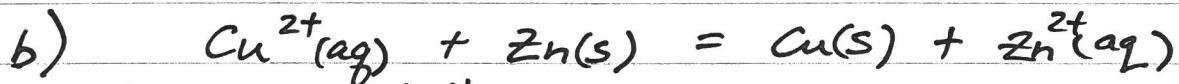
$K = \dfrac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \approx \dfrac{m_{Zn^{2+}}}{m_{Cu^{2+}}}$ assuming ideal solution behavior

$1.770 \times 10^{37} = \dfrac{m_{Zn^{2+}}}{m_{Cu^{2+}}} = \dfrac{x}{0.250 - x} = $ huge number!

∴ $0.250 - x \approx 0$ $x = \boxed{0.250 \text{ mol kg}^{-1}} = m_{Zn^{2+}}$

$m_{Cu^{2+}} = \dfrac{m_{Zn^{2+}}}{K} = \dfrac{0.250 \text{ mol kg}^{-1}}{1.770 \times 10^{37}} = \boxed{1.41 \times 10^{-38}\ m_{Cu^{2+}}}$ $\left.\begin{array}{c} \text{only} \\ 1\ Cu^{2+} \\ \text{ion in} \\ 1.14 \times 10^{14} \\ \text{kg water!} \end{array}\right.$

to remove Cu^{2+} ions from solution,
use powdered Zn metal
        ↖ large surface area to bind Cu